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Birefringent Optical Properties in Cadmium Halide Single Crystals

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Ordinary and extraordinary refractive indices of $CdCl_2$, $CdBr_2$ and CdI_2 single crystals were measured at room and liquid nitrogen temperatures in the region from 7000 A to the shorter wavelength up to the absorption edge. The measurement was carried out by a "two-angle" interference method in which both indices could be determined together with the thickness of the sample crystal. The results were related to optical absorption. Dispersion behaviors of the indices in the energy region well below the optical gap could be analyzed using a single-effective-oscillator model.

1. Introduction

Cadmium halides other than fluoride crystallize in a typical layer structure with highly ionic property. An increasing amount of optical studied has been carried out on these materials in the last decade,[1-12] because of the interest in the characteristics due to the layer structure. The measurement of the refractive index has been carried out by Tubbs on CdI_2.[13-14] His data however lack the values of the extraordinary-ray refractive index near the absorption edge. As for $CdCl_2$ and $CdBr_2$, any reliable data has not been reported on the refractive indices.

In the present work, the ordinary and extraordinary refractive indices of $CdCl_2$, $CdBr_2$ and CdI_2 single crystals are measured at room temperature (RT) and liquid nitrogen temperature (LNT) in the region from 7000 A to the shorter wavelength up to the absorption edge. The measurements were carried out by a "two-angle" interference method described in sections 2 and 3. This method allows one to determine

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the refractive index without any direct measurement of the sample thickness, and therefore is effective to determine the thickness of thin crystals whose refractive index is unknown. the refractive indices obtained are directly related to the intensity and position of electronic absorption bands. The dispersion behaviors in the energy region well below the optical gap are analyzed using the single-effective-oscillator model of Wemple and Didomenico.[15)]

2. "Two-Angle" Interference Analysis for Determining the birefringent Refractive Index

The ordinary and extraordinary refractive indices of the cadmium halides were determined from interference data through a "two-angle" interference analysis described in the following.

When a monochromatic light wave of wavelenght λ and intensity $I^{(i)}$ is incident at an angle ϕ on a thin isotropic crystal with two parallel surfaces, the intensities of the reflected ($I^{(r)}$) and transmitted ($I^{(t)}$) light are known to be given by

$$I^{(r)} / I^{(i)} = F \sin^2 \frac{\delta}{2} / \left(1 + F \sin^2 \frac{\delta}{2} \right), \tag{1}$$

$$I^{(t)} / I^{(i)} = \left(1 + F \sin^2 \frac{\delta}{2} \right)^{-1} \tag{2}$$

with

$$F = 4R/(1+R)^2, \tag{3}$$

$$\delta = (4\pi d/\lambda)\sqrt{n^2 - \sin^2\phi}, \tag{4}$$

where R, n and d are the surface reflectivity, the refractive index and the thickness of the crystal respectively. The quantity δ is the phase difference concerning to the interference. In the case of the uniaxial crystal with the two surfaces perpendicular to the optical c axis, eq.(4) gives the phase difference for ordinary ray (O-ray) δ_o if n is replaced by the refractive index for O-ray $n_\perp$. The phase difference for extraordinary ray (E-ray) δ_e is shown to be related to the E-ray refractive index $n_\parallel$ by

$$\delta_e = (4\pi d/\lambda)(n_\perp / n_\parallel)\sqrt{n_\parallel^2 - \sin^2\phi} \ . \tag{5}$$

The condition of maximum transmission (or minimum reflection) is

therefore given by the formulae

$$\frac{m_o \lambda}{2d} = \sqrt{n_\perp^2 - \sin^2\phi} \qquad \text{for O-ray,} \tag{6}$$

and

$$\frac{m_e \lambda}{2d} = (n_\perp / n_\parallel)\sqrt{n_\parallel^2 - \sin^2\phi} \qquad \text{for E-ray,} \tag{7}$$

where m_o and m_e are the orders of interference for O-ray and E-ray respectively, m_e being equal to m_o at $\phi = 0$. Treating m_o and m_e as functions of λ and ϕ : $m_o = m_o(\lambda, \phi)$ etc., and letting $m_o(\lambda_i, 0) = m_e(\lambda_i, 0) = m + p_i$, $m_o(\lambda_i, \phi) = m + q_i$ and $m_e(\lambda_i, \phi) = m + r_i$ $(i = 1, 2)$, where m is an integral part of $m_o(\lambda_1, 0) = m_e(\lambda_1, 0)$ and thus p_1 is a decimal fraction, we obtain

$$m = -\frac{1}{2}\,\frac{(p_1^2 - q_1^2)\lambda_1^2 - (p_2^2 - q_2^2)\lambda_2^2}{(p_1 - q_1)\lambda_1^2 - (p_2 - q_2)\lambda_2^2} \tag{8}$$

and

$$d = \frac{\lambda_1}{2\sin\phi}\sqrt{(p_1 - q_1)(2m + p_1 + q_1)}\,. \tag{9}$$

Since the shifts of the order of interference p_1, q_1, p_2 and q_2 can be determined by measuring the ϕ-dependence of the interference order at two different wavelengths (λ_1 and λ_2) and the λ-dependence of the interference order at a nonzero incident angle (ϕ) as will be described in the next section, the values of d and m can be determined with the use of eqs.(8) and (9). Once m and d are determined, the O-ray index $n_\perp(\lambda)$ at an arbitrary wavelength λ are computed using the formula

$$n_\perp(\lambda) = \left[\left(\frac{\lambda}{2d}\right)^2 (m+q)^2 + \sin^2\phi\right]^{1/2}, \tag{10}$$

where the values of $m+q = m_o(\lambda, \phi)$ are given by the λ-dependence data for O-ray. On the other hand, the E-ray refractive index $n_\parallel(\lambda)$ can be determined from the E-ray data on $m+r = m_e(\lambda, \phi)$ using the values of $n_\perp(\lambda)$:

$$n_\parallel(\lambda) = \frac{n_\perp^2 \sin^2\phi}{n_\perp^2 - \left(\frac{\lambda}{2d}\right)^2 (m+r)^2}\,. \tag{11}$$

3. Experimental Procedures

Single crystals of $CdCl_2$, $CdBr_2$ and CdI_2 were grown from the melt by the stockbarger technique. Crystal platelets of about 2x5 mm^2 in area and about 5~50μ in thickness were prepared by simply cleaving these crystals, and were mounted on the sample holder of a metal cryostat.

The monochromatic light was incident at an arbitrary angle ϕ on the sample surface perpendicular to the c axis. The light illuminating the sample was linearly polarized by a Rochon polarizer placed in front of the light source composed of a 500W xenon lamp (in the wavelength region of 7000-2500 A) and a 200W deuterium lamp (in the shorter wavelength region), and was chopped at the frequency of about 86 Hz by a cylindrical beam chopper inside the monochromator. All the optical measurements were carried out using the double beam detection system reported in ref. 16.

The wavelength λ_1 at which the shifts of the interference order p_1, q_1 and r_1 of eqs.(8)-(9) are to be determined was fixed at 6000 A. On the other hand the wavelength λ_2 at which the parameters p_2, q_2 and r_2 are to be determined was fixed near the absorption edge, so as to minimize the experimental error in the measurement of m by introducing a spacing between the λ_1 and λ_2 in eq.(8) as large as possible (λ_2=2450 A in $CdCl_2$, λ_2=2700 A in $CdBr_2$ and λ_2=3700 A in CdI_2).

At each wavelength of λ_1 and λ_2, the change in the order of transmission interference of the sample with respect to the change in the incident angle ϕ was measured for O-ray and E-ray in the range between $\phi = 0$ and $\phi = 50°$. The relative interference-orders corresponding to the successive transmission maxima were plotted against $\sin^2\phi$. From an appropriate interpolation of these plots were obtained the quantities $q_1 - p_1$, $r_1 - p_1$, $q_2 - p_2$ and $r_2 - p_2$ at $\phi=45°$ together with the decimal part p_1. In the next place the λ-dependence of the interference order for O-ray and E-ray was measured at $\phi=45°$ in the region from 7000 A to the shorter wavelength up to the absorption edge. This measurement was carried out by recording the periodic change (with respect to λ) in the intensity ratio of the transmitted light to the reflected light. An example of the trace of the periodic change is shown in Fig.1. Then the quantities $q-q_1$ and $r-r_1$ were easily obtained as a function of λ by interpolating the plots of the change in the interference order against the invers of the photon energy. (The nonlinearity of these plots was an

appropriate measure of the dispersion.) The decimal parts of q_i and r_i $(i = 1,2)$ determined from the λ-dependence data agree well with those determined from the φ-dependence data. From these data the values of q and r were obtained as a function of λ, and therefore the values of p_2, q_2 and r_2 could be determined together with the values of q_1 and r_1.

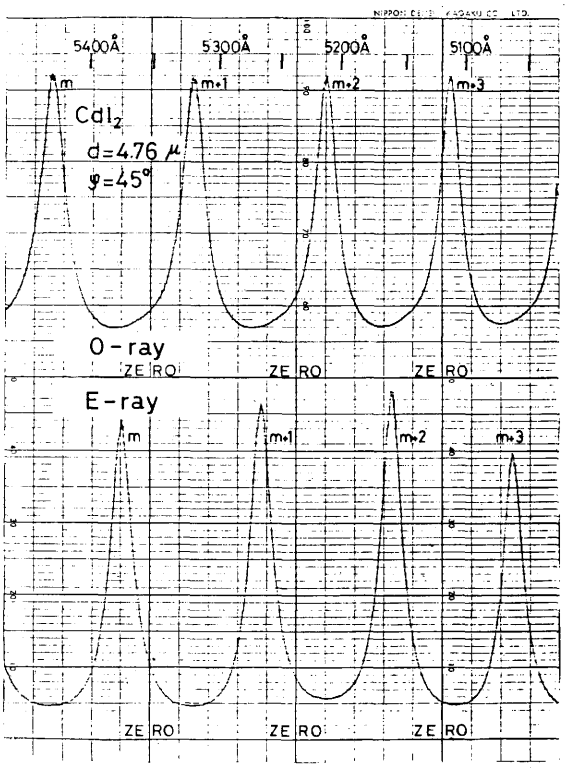

Fig. 1 An example of interference spectra for O-ray (upper part) and E-ray (lower part) obtained by measuring the periodic change in the intensity ratio of the transmitted light to the reflected light with respect to wavelength. The maximum-to-minimum ratio is about 6 for O-ray and about 9 for E-ray.

4. Experimental Results

The variations of the O-ray and E-ray refractive indices ($n_\perp$ and $n_\parallel$ respectively) with wavelength for the single crystals of $CdCl_2$, $CdBr_2$ and CdI_2 are illustrated by Fig.2. The values of the indices should be accurate within the experimental errors of 1 %. It is noteworthy that the close agreement is achieved between the refractive indices of CdI_2 (at RT) shown in Fig.2 and those reported in ref.14 which were based on photographic measurements of interference frings for crystals whose thickness were determined by using a polarizing microscope.

As is evident from Fig.2, the cadmium halide crystals other than fluoride show a high birefringence due to their layer structure, and the optical characteristics of the negative uniaxial crystal. The indices $n_\perp$ and $n_\parallel$ increase with increasing halogen atomic number of compounds as in the case of most ionic halides such as alkali halides. When the crystals are cooled from RT to LNT these indices increase by

less than 1 % at the long wavelengths. The most prominent change is the blue shifts of the absorption edges resulting in the larger indices at RT than the indices at LNT in the short wavelengths. In fact the blue shifts were observed for all the materials in the transmission measurements. The refractive indices of $CdCl_2$ and $CdBr_2$ near the absorption edges show

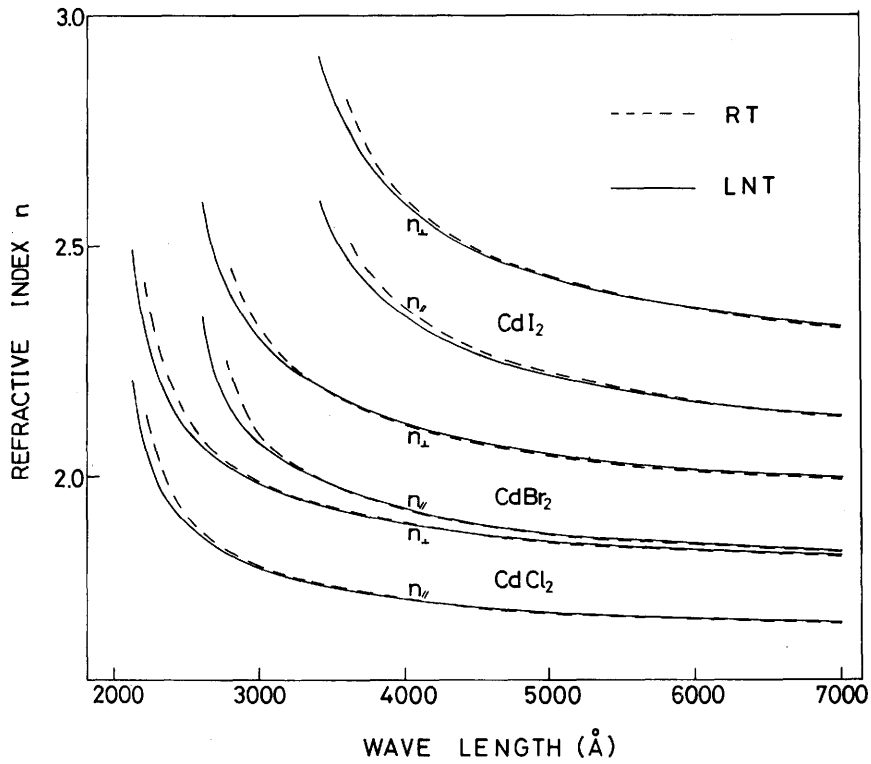

Fig. 2 Birefringent refractive index against wavelength for $CdCl_2$, $CdBr_2$ and CdI_2 measured at RT and LNT in the region from 7000 A to the shorter wavelength up to the absorption edge.

a large dispersion for E-ray compared with the dispersion for O-ray. This means that the mechanism of the optical absorption occurring just above the threshold is highly dichroic with a large E-ray absorption coefficient compared with the O-ray one. As for the CdI_2 crystal, however, no clear difference between the dispersion for O-ray and that for E-ray is observed near the absorption edge.

It is useful to compare the values of $n_\perp$ shown in Fig.2 with those obtained from the reflectivity for normal incident light, $R = (n_\perp - 1)^2/(n_\perp + 1)^2$, in a non-absorbing region. The reflectivity measurements of freshly cleaved surfaces of CdI_2 and $CdBr_2$ crystals

(at wavelengths near the absorption edges) give values of $n_\perp$ that agree with those of Fig.2 within the experimental errors of 2 %. The values of $n_\perp$ of $CdCl_2$ obtained from the reflectivity measurements were smaller than those shown in Fig.2 by about 5 %. This seems to be due to the reduction of the reflectivity during exposure of the cleaved faces to air since the $CdCl_2$ samples are highly hygroscopic.

5. Discussion

In materials exhibiting a band gap, the dispersion behavior in the region of photon energy below the gap is related to an absorption process according to the requirement of causality. Using an electronic-dipole oscillator model, the dispersion of the refractive index n is expressed by

$$n^2 - 1 = \frac{4\pi\hbar^2 e^2 N}{m} \sum_i \frac{f_i}{E_i^2 - E^2} \quad , \tag{12}$$

where m is the electron mass, N is the number of molecules per unit volume, E is photon energy, and E_i is the energy of the electronic-dipole oscillator having the strength f_i. To discuss the dispersion of the refractive indices of the cadmium halides shown in Fig.2 in terms of a few oscillators, the first oscillator (of the lowest energy) is isolated and the remaining ones were combined into a single "effective" oscillator. Then eq.(12) yields a two-oscillator model of the form

$$n^2 - 1 = \frac{4\pi\hbar^2 e^2 N}{m} \left(\frac{F_{eff}}{E_{eff}^2 - E^2} + \frac{f_1}{E_1^2 - E^2} \right), \tag{13}$$

where the "effective" oscillator energy E_{eff} ($> E_1$) and the "effective" oscillator strength F_{eff} are related straightforwardly to all the f_i and E_i of the higher order oscillators ($i > 1$). The first term represent the dominant contribution of the optical absorption (above the gap) to the refractive index n in the energy region well below the gap. The second term may contribute to n mainly in the region near the gap. In the following discussion a convention is used such that, whenever one is concerning with the direction of the polarization of the light in the absorption process, the quantities n, E_{eff}, E_1, F_{eff} and f_1 in eq. (13) are replaced by $n_\perp$, $E_{eff\perp}$, $E_{1\perp}$, $F_{eff\perp}$ and $f_{1\perp}$ respectively for O-ray and by $n_{//}$, $E_{eff//}$, $E_{1//}$, $F_{eff//}$ and $f_{1//}$ respectively for E-ray.

It can be shown that the two-oscillator model is effective to explain the dispersion behaviors of the cadmium halide crystals shown in Fig.2. The large dispersion for E-ray compared with that for O-ray, which is observed near the absorption edge in $CdCl_2$ and $CdBr_2$, is attributable to the dichroic strength of the first oscillator: $f_{1\perp} < f_{1//}$ with $E_{1\perp} \sim E_{1//}$. This is consistent with the previous prediction:[11] the E-ray optical transition probability of the first absorption band of $CdCl_2$ and $CdBr_2$ exceeds the O-ray one on account of a strong crystal field parallel to the optical c axis. As for the CdI_2 crystal the difference in the values between $f_{1//}$ and $f_{1\perp}$ seems to be small, since no clear difference in the dispersions between $n_{//}$ and $n_{\perp}$ is observed near the edge. On the oter hand, in order to explain the negative birefringent behavior observed in $CdCl_2$, $CdBr_2$ and CdI_2 over the long wavelength range, the "effective" oscillator must be assumed to be more dichroic with a fairly large oscillator strength for O-ray compared to that for E-ray. The origin of the negative birefringent property of the layer cadmium halide crystals is therefore different from that of a typical negative birefringent crystal such as calcite; in the calcite the negative birefringence in the transparent region is based on the first strong absorption band observed only for O-ray.[17]

Figure 3 shows plots of the value $(n^2-1)^{-1}$ against the square of the photon energy (in eV) for $CdCl_2$ at LNT. A linearity is observed over a considerably extended range in the low energies. Similar results are also obtained for all the dispersion curves of $CdBr_2$ and CdI_2. These facts, to-

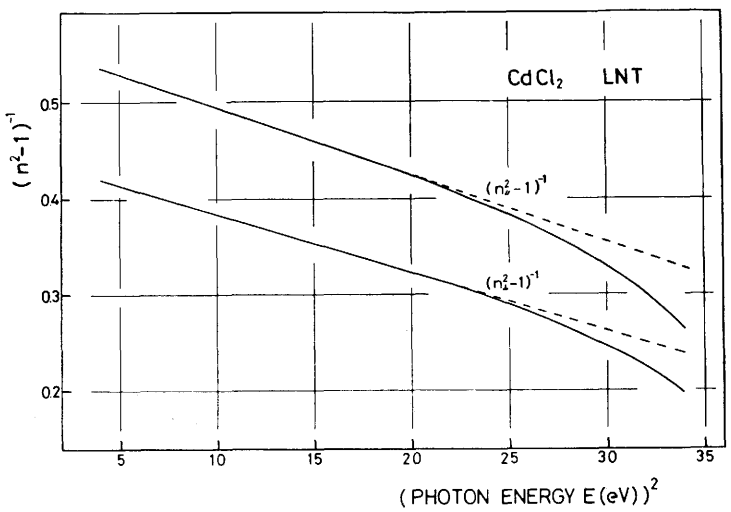

Fig. 3 Plots of the values $(n^2-1)^{-1}$ for $CdCl_2$ at LNT against the square of the photon energy for O-ray and E-ray. The dashed lines show single-effective-oscillator fits of the form of eq.(14) with the values of the parameters given in Table I.

gether with the dichroic nature of the first oscillator strength, i.e., $f_{1//} \geq f_{1\perp}$, indicate that the dominant contribution to the refractive indices at the low energies of the cadmium halides comes, in fact, from the "effective" oscillator, since otherwise the values of $n_{//}$ should exceed the values of $n_{\perp}$ (see eq.(13)). Deviations from the linearity at the high energies are attributed to the first oscillator.

In isotropic materials, the dispersion behaviors below the interband absorption edge have been successfully analyzed in ref.15 using a single-effective-oscillator model of the form

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} , \qquad (14)$$

where E_d is the dispersion energy which is a measure of the strength of interband optical transitions, and E_0 is the single oscillator energy equivalent to the parameter E_{eff} in eq.(13). As is suggested in the last paragraph, a single-oscillator representation appears to be effective for the cadmium halides in the energy region well below the gap. It is tempting, therefore, to analyze the results shown in Fig.2 using eq.(14). Optimum fits in the energy region sufficiently below the threshold are obtained with the values of the parameters $E_{d\perp}$, $E_{d//}$, $E_{0\perp}$ and $E_{0//}$ given in Table I. (The parameters E_d and E_0 in eq.(14) are replaced by $E_{d\perp}$ and $E_{0\perp}$ respectively for O-ray, and by $E_{d//}$ and $E_{0//}$ respectively for E-ray.) The threshold energy $E_{t\perp}$ obtained for O-ray from the transmission measurements and the ratio $E_{0\perp}/E_{t\perp}$ are also given in the last two columns of the table.

It has been reported in ref.15 that, in isotropic materials, the

Table I. O-ray and E-ray single-oscillator parameters of $CdCl_2$, $CdBr_2$ and CdI_2 at LNT. In the table are also given the O-ray single-oscillator parameters for BiI_3 reported in ref.18 and those for PbI_2 determined from the refractive index data reported in ref.14.

	$E_{d\perp}$ (eV)	$E_{d//}$ (eV)	$E_{0\perp}$ (eV)	$E_{0//}$ (eV)	$E_{t\perp}$ (eV)	$E_{0\perp}/E_{t\perp}$
$CdCl_2$	19.2	15.9	8.5	9.0	5.6	1.53
$CdBr_2$	19.9	16.3	7.1	7.3	4.8	1.48
CdI_2	23.1	18.7	5.8	5.8	3.6	1.61
PbI_2	19.4		3.8		2.4	1.58
BiI_3	17.2		3.1		1.9	1.63

parameters E_0 and E_d obey two simple empirical rules. The first is that the oscillator energy E_0 is related to the threshold energy E_t by $E_0/E_t \sim 1.5$. The second rule is concerned with the dispersion energy and is stated in the form $E_d = \beta N_c Z_a N_e$, where N_c is the coordination number of the cation nearest neighbor to the anion, Z_a is the formal chemical valency of the anion, N_e is the effective number of valence electrons per anion, and β is a essentially two-valued coefficient ranging between a lower limit, i.e., an "ionic" limit, and a higher limit, i.e., a"covalent" limit.

As is shown in Table I, each of the ratio $E_{0\perp}/E_{t\perp}$ of the cadmium halides is close to the 1.5. Similar results are also obtained for E-ray using the same values of $E_{t//}$ as the values of $E_{t\perp}$.* Therefore the empirical rules found in the isotropic materials seem to be applicable to the cace of the cadmium halides. The values of the parameters $E_{d\perp}$ of $CdCl_2$ and $CdBr_2$ are close to each other. Compared with these values, the CdI_2 crystal shows a relatively large value of $E_{d\perp}$. Similar arguments hold for E-ray. Therefore the value of the coefficient β in CdI_2 is larger than that in $CdCl_2$ and $CdBr_2$, since each of the values of N_c, Z_a and N_e for CdI_2 are equal to the corresponding value for $CdCl_2$ and $CdBr_2$. It can thus be stated in terms of the second rule mentioned above that the CdI_2 crystal shows a certain covalency.

In Table I are also given the single-oscillator parameters for BiI_3 reported in ref.18** and those for PbI_2 determined from the refractive index data reported in ref.14. The values of the ratio $E_{0\perp}/E_{t\perp}$ for these compounds are compared favorably with the 1.5 again. The value of the parameter $E_{d\perp}$ of PbI_2 together with that of $CdCl_2$ and $CdBr_2$ suggests the "ionic" limit of the O-ray dispersion energy for the layer di-halides. The bismus tri-iodide however shows a small value of $E_{d\perp}$ compared with these compounds. This difference seems to be attributable to the difference in N_c, the coordination number of the cation nearest neighbor to the anion. In fact the value $E_{d\perp} = 17.2$ in BiI_3, if multiplied by 3/2, exceeds

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* According to our recent data on the optical reflectance measurements, the peak energies of the first absorption bands for E-ray are nearly equal to those for O-ray.

** Single-oscillator parameters are also given in ref. 18 for CdI_2 and PbI_2. However these values are based on the "apparent" refractive index data of ref. 13.

even the value in CdI_2 possibly due to the difference in the covalency.

The causality requirement of the radiation process gives a direct relationship of the parameters E_0 and E_d to the imaginary electronic dielectric function $\varepsilon_2(E)$: [15]

$$E_0^2 = M_{-1} / M_{-3} \ , \tag{15}$$

$$E_d^2 = M_{-1}^3 / M_{-3} \ , \tag{16}$$

where M_r is the rth moment of $\varepsilon_2(E)$ defined by

$$M_r = \frac{2}{\pi} \int_{E_t}^{\infty} E^r \varepsilon_2(E) \, dE \ . \tag{17}$$

Therefore the values of the parameters E_0 and E_d can be computed using the reflectance spectrum from which the $\varepsilon_2(E)$ spectrum is obtained through the kramers-kronig analysis. The values of $E_{0\perp}$ obtained from the O-ray reflectance spectra measured up to about 12 eV for $CdCl_2$, $CdBr_2$ and CdI_2 are close to those shown in Table I within the difference of 10 %. (In the computations the high energy part of the integration in eq.(17) was truncated at 12 eV.) On the other hand the computed values of the dispersion energy $E_{d\perp}$ are smaller than those of Table I by 20-50 %. This can be attributed to the truncated integration in eq.(17), since the value of M_{-1} is more sensitive to the high-energy $\varepsilon_2(E)$ spectrum than the value of M_{-3} .

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